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Reversible Electric Current Switching at the Normal Metal – $Bi_2Sr_2CaCu_2O_{8+y}$(001) Heterojunction

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We have studied the electronic instability of $Bi_2Sr_2CaCu_2O_{8+y}$-based heterojunctions affected by an electric field. According to experimental results the instability is dictated by a change in the number of carriers in the surface depleted layer under the influence of the electrical field. The current-voltage characteristics of the $Bi_2Sr_2CaCu_2O_{8+y}$ – normal metal heterojunctions have been investigated at room and liquid helium temperatures.

1. Introduction

The nature of excess carriers introduced into the cuprates electronic system by doping is one of the key factors in formation of the normal state and superconductive properties of high temperature superconductors (HTSCs). In this work we continue to study the hysteresis effect observed earlier [1,2] at the normal metal – $Bi_2Sr_2CaCu_2O_{8+y}$ interface. An electric field of unlike polarity stimulates two resistive states of the (001) single crystal surface, conductive (low resistive state, LRS) and low conductive (highly resistive state, HRS).

2. Sample preparation and experimental details

Heterojunctions (inset(a) in Fig. 1 were fabricated by the technique described in Ref. [2]: The counter electrode was either an Ag needle (the rounding-off radius is 0.1 mm) or a silver film deposited onto freshly cleaved $Bi_2Sr_2CaCu_2O_{8+y}$ (001) surface.

The cleavage surface and its aging in air were examined by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). For spectroscopic studies crystals were cleaved in ultrahigh vacuum chamber of electron

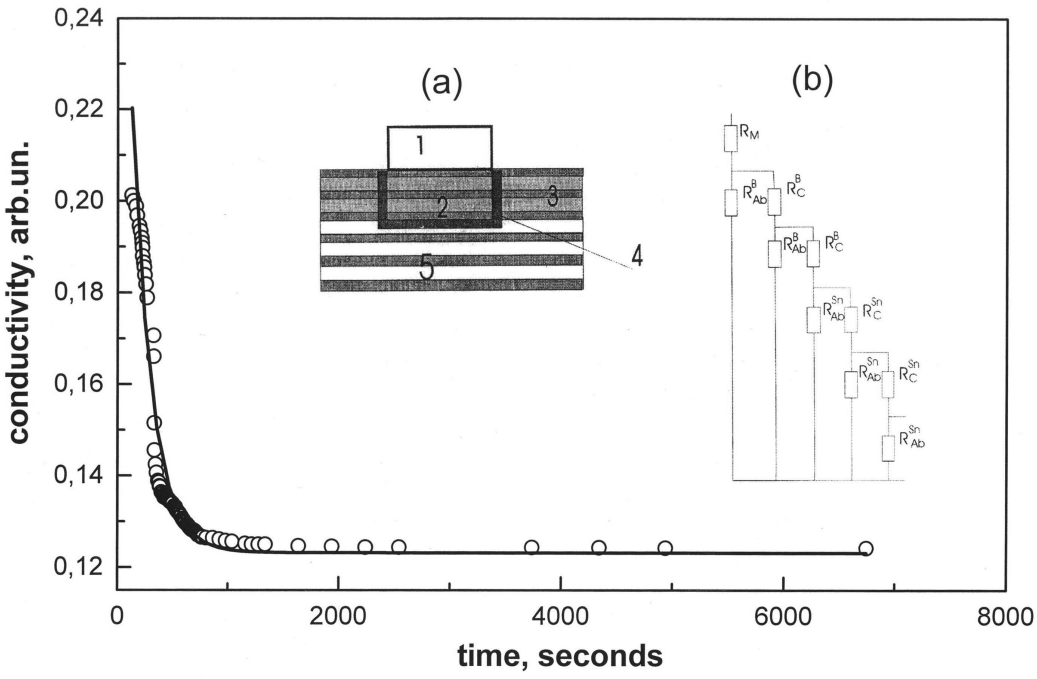

Figure 1. Time dependence of the point contact conductance. Inset (a) – contact, schematic: (1) metalic electrode, (2) degraded surface region under the contact, (3) degraded surface region of the single crystal, (4) transition layer between the degraded region and the bulk part of the crystal, (5) bulk non-degraded crystal part. Inset (b) – equivalent contact scheme.

spectrometer ESCALAB-5 provided with spherical sector energy analyzer. After AES and XPS spectra had been taken from the freshly cleaved surface, the sample was aged at normal atmospheric pressure for 1, 2, 5 min, 1 hour, and 60 hours. After each consequent air exposure the sample was taken back into the analytic chamber for measurements.

3. Results and discussion

Conductivity measurements showed that the HTSC–normal metal junction is "alive" immediately after cleavage due to degradation and, possibly, charge reconstruction of the surfaces both under the contact and outside it (inset (a) in Fig. 1, regions 2 and 3): the conductivity drops with aging time by approximately exponential law (Fig. 1). The time constant is about several minutes.

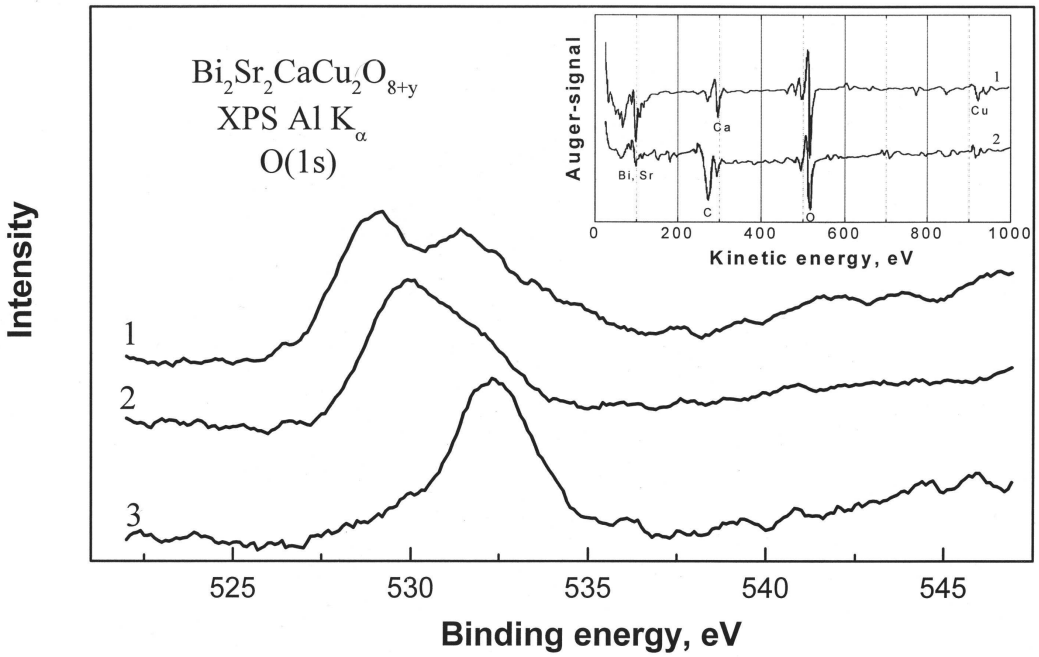

Figure 2. XPS spectra of O(1s) core level: (1) – freshly cleaved surface, (2) – degraded surface after Ar^+-bombardment, (3) – degraded (exposed to air for 5 minutes) surface. Inset: AES spectra recorded in the dN/dE mode ($E_p = 3$ keV) from clean (1) and degraded surface (2).

Main changes in surface composition occur also in the first minutes of the degradation. The latter is confirmed by AES and XPS data presented in Fig. 2. The degraded surface AES spectrum (curve 2, inset in Fig. 2) demonstrates attenuation of Ca (290 eV) and Cu (770–920 eV) signals as well as changing within 50–100 eV range where Bi and Sr peaks are located. The appearance of the peak in the vicinity of 270 eV suggests the carbon adsorption. Note that the difference between AES-spectra recorded at aging times of 5 minutes and 60 hours was insignificant.

XPS studies show that the cleavage surface aging at atmospheric pressure changes appreciably the O(1s) core-level structure and does not practically change spectra of Bi, Ca, and Cu core levels. O(1s) spectrum of the clean surface (curve 1 in Fig. 2) demonstrates the overlapping features corresponding to the oxygen atoms in the Sr-O, Cu-O, and Bi-O (529–531 eV) layers [3]. Upon aging in air (curve 3 in Fig. 2), the O(1s) spectrum shifts to higher binding energies (the peak maximum at 532.5 eV) suggesting a change in the oxygen atom states in the near-surface layers. This shift may be caused by occupa-

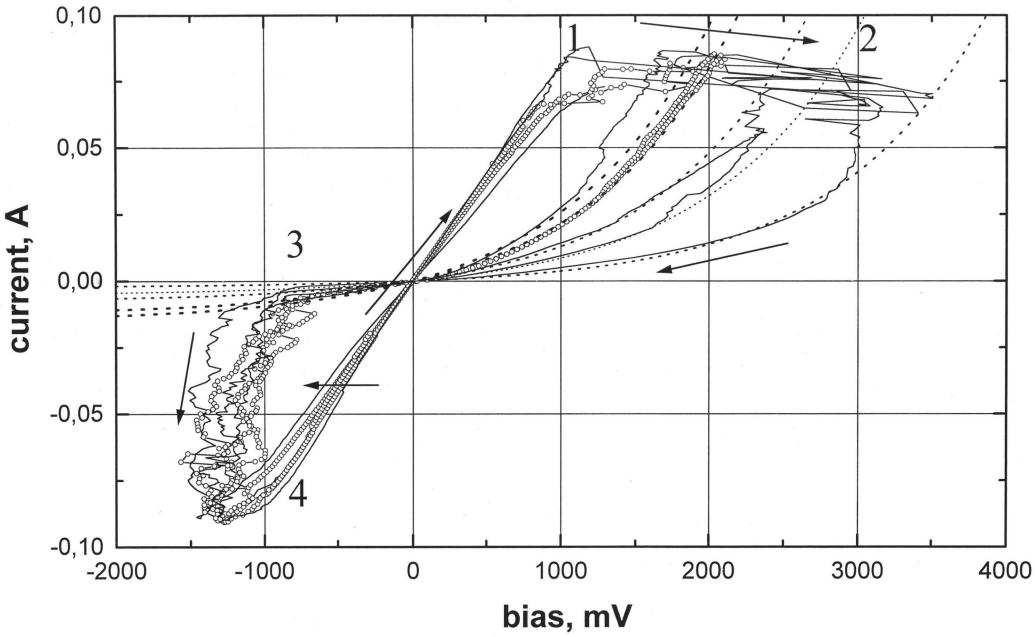

Figure 3. Examples of heterojunction IVCs at different voltage levels. Open circles are experimental data. Dashed lines are fit data: $I = 0.075n \exp(0.001V - 1)$, where $n = 35, 15, 10, 6, 5$.

tion of vacancies in the surface Bi-O layer and by the formation of some new compounds (for example, peroxides, hydroxiles, or carbonates) in the degraded sample part. Ar^+ sputtering of the contaminated surface (removal of 50–70 Å thick layer from the sample top) shifts the O(1s) spectrum back to lower binding energies. One can assume from this fact that the depth of the degraded layer has the order of several tens of Å.

Figures 3–5 display the principal results of this paper related to the influence of the applied electric fields on the contact properties. Fig. 3 gives a typical example of the I-V characteristic (IVC) of the junctions for different levels of the voltage sweep at $T = 300$ K. To obtain the reproducible results of current switching effects one should apply the positive voltage (positive on the single crystal) of the order of 1 V for several minutes (point 1 in Fig. 3). After that, applying higher voltages (from point 1 to point 2 in Fig. 3) one can cause the transition from the LRS to one of the branches of the HRS (point 2 → point 3). At negative voltages of the order of 1 V the reverse transition from HRS to LRS branch takes place (point 3 → point 4 in Fig. 3). The main voltage

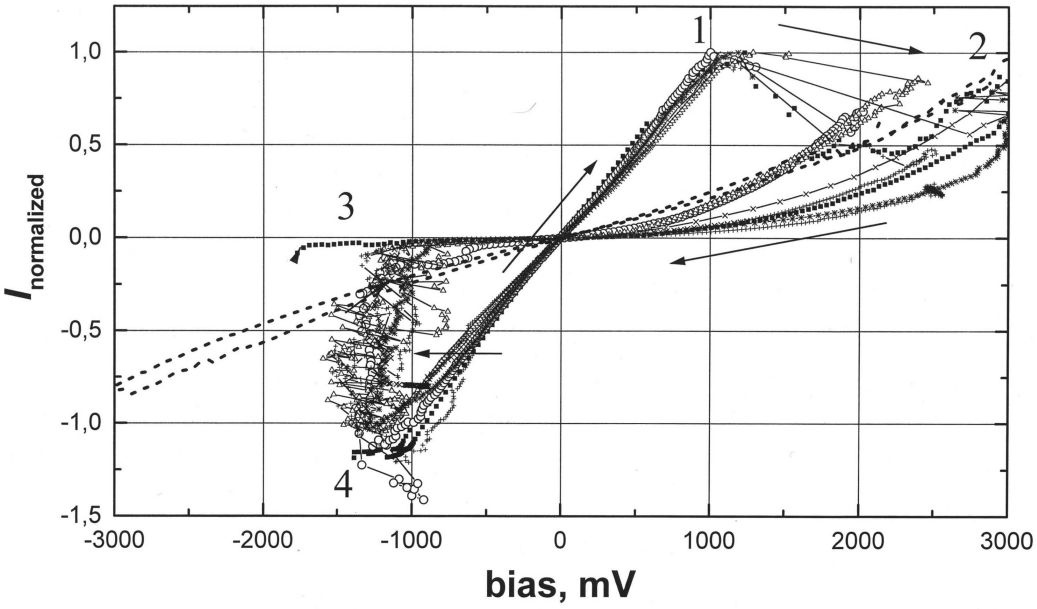

Figure 4. Current-normalized IVCs of heterojunctions with different surface layer resistivities. $I_{norm} = I(V)/I_{max}$, where I_{max} is the maximal current value in the particular junction. Squares: $I/I_{max} = 4330$; circles: $I/I_{max} = 306$; triangles: $I/I_{max} = 35$; crosses: $I/I_{max} = 11$.

governing the resistive state of the heterojunction is the voltage $+V_2$ (+ on the single crystal). The higher this voltage ($+V_2$), the more ohmic is the highly resistive phase. The IVC of HRS junctions is approximated by the dependence

$$I = I_0 n(\exp(V/V_0) - 1).$$

that is characteristic of Schottky diodes [4]. Fig. 4 illustrates the normalized I_{norm}-V curves for junctions of different resistivities. It is seen that the hysteresis effect is of universal character, immune from the thermal influence of the current, and is of intrinsic nature.

It is important to mention that only positive voltage on the single crystal can induce transition from LRS state to HRS that gives a possibility to observe a hysteresis effect. So, an electric field concentrated at the normal metal–HTSC interface (intensity of the electric field up to 10^5 V/cm) forces negative charges out of the contact region to the periphery and stimulates the change of the conductivity character of the below-the-contact region.

When the degraded layer becomes extended enough (several tens of Å), the effect of the electric field on the IVC of contacts is absent (Fig. 4, dashed

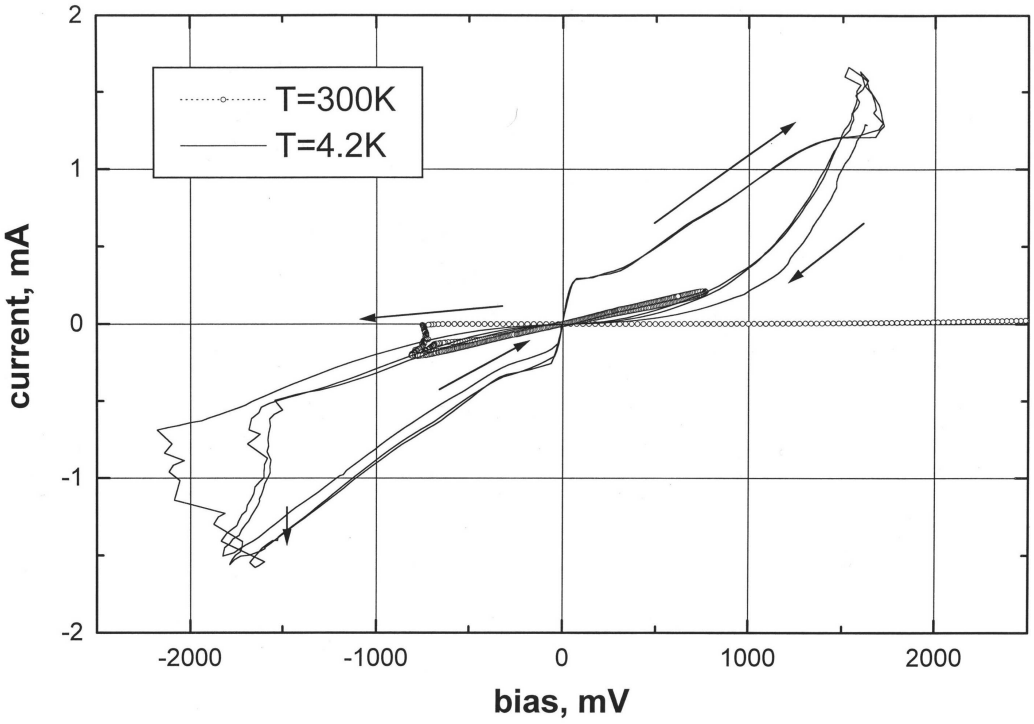

Figure 5. IVCs of the $Bi_2Sr_2CaCu_2O_{8+y}$ – normal metal heterojunction at 4.2 K and 300 K.

line) and only highly resistive states exist. So, the transport properties of the contact (current switching) are only affected by the electric field when the current spreads into the inner near contact layers.

The temperature effect on the IVCs of the contact is more complicated since in addition to the temperature, other factors affect the properties of the contacts. However, reversible current switching effect could be observed after sample cooling down to 4.2 K. Even at helium temperatures the applied electric field drives the contact from the metallic (with the manifestation of superconductivity) to the highly resistive state. Fig. 5 illustrates the IVCs of the contact at room and helium temperatures.

Note that at room and helium temperatures both phases, LRS and HRS, are bistable and reproducible: the voltage alone drives the heterocontact from one to the other state. Two scenarios of the observed current switching phenomenon can be proposed:

1) carrier concentration changes in CuO_2 planes due to electric field stimulated diffusion of oxygen ions into the degraded surface region,

2) phase separation under the influence of the electric field in mixed valence systems.

In the first scenario (supported by spectroscopic data) application of the corresponding electric field initiates the diffusion of oxygen ion subsystem in BiO_2-SrO blocks that can directly or indirectly change the carrier concentration in CuO layers and switch between HRS and LRS. XPS O($1s$) core level spectra confirm that oxygen atoms are quite labile and first to change upon surface degradation. Note that during spectroscopic measurements the electron beam stimulated diffusion of oxygen ions was observed. According to our AES data, exposure of the $Bi_2Sr_2CaCu_2O_{8+y}$ (001) clean cleaved surface to the electron beam (E_p = 3 keV) for several minutes was necessary to obtain reproducible spectra with good signal to noise ratio and without charging effects. At the same time, exposure to incident electron beam induced slight changes of oxygen concentration in the area of the electron beam. Similar effects were observed during diffraction experiments: we could notice changes in the quality of low energy electron diffraction pattern for samples exposed to electron beam (E_p = 30–60 eV). Diffraction pattern improvement under the beam suggests additional ordering of surface oxygen atoms.

The second possible scenario is a phase separation in the junction area under the influence of an electric field. A number of runs show a direct dependence of transport and thermodynamic properties of HTSC on the charge state in CuO_2 and the tendency of a weakly doped system to a frustrated phase separation to metallic phase and hole depleted antiferromagnetic phase [5] under the influence of various factors. The occurrence of easily diffusing dopants (oxygen ions) stimulates the system decomposition onto two-phase state: metallic phase (domains) and dielectric phase depleted in carriers. The authors of Ref. [6] showed that at elevated temperature (700°C) and electric field strength of $2 \cdot 10^2$ V/cm, negatively charged oxygen ions move into YBCO (phase 123). In our case great enough electric field develops at the contact boundary. This field stimulates the migration of negatively charged ions. The phase separation is an electron-assisted process so that the relevant times have to be short. The long times observable in our case are likely to be related to the ion diffusion times.

4. Conclusions

In summary, the electronic instability of $Bi_2Sr_2CaCu_2O_{8+y}$–normal metal heterojunctions has been investigated. The effect of reversible electric current switching in these heterojunctions was observed at room and helium temperatures. It was shown that the effect of the current switching is due to the influence

of the electric field on mobile negative charges in a depleted near-surface layer of the single crystal: positive voltage on the single crystal causes first transition from low to highly resistive state. Long characteristic times and spectroscopic data suggest that the principal factor responsible for this switching between two resistive states is the electric field stimulated diffusion of the labile oxygen ion subsystem.

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